



TITLE:

Effects of Gamma Radiation on Polymer in Solution. (IX) : A Turbidimetric Study on Solution of Poly(Vinyl Alcohol) Irradiated below Critical Concentration for Gel-Formation (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, VII)

AUTHOR(S):

Sakurada, Ichiro; Ikada, Yoshito

CITATION:

Sakurada, Ichiro ...[et al]. Effects of Gamma Radiation on Polymer in Solution. (IX) : A Turbidimetric Study on Solution of Poly(Vinyl Alcohol) Irradiated below Critical Concentration for Gel-Formation (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, VII). Bulletin of the Institute for Chemical Research, Kyoto Un ...

ISSUE DATE:

1966-03-31

URL:

<http://hdl.handle.net/2433/76107>

RIGHT:

Effects of Gamma Radiation on Polymer in Solution. (IX)

A Turbidimetric Study on Solution of Poly(Vinyl Alcohol) Irradiated below Critical Concentration for Gel-Formation

Ichiro SAKURADA and Yoshito IKADA*

Sakurada Laboratory, Institute for Chemical Research, Kyoto University

Received January 12, 1966

The radius of micro-gel particles formed at the irradiation of dilute aqueous solution of PVA was estimated by turbidity measurement and supplementarily by electron micrographs. The radius calculated from the turbidity was in the range from 500Å to 2400Å depending on radiation dose, polymer concentration at irradiation and degree of polymerization of sample. It was found that the dimension of micro-gel particle became smaller as irradiation proceeded. This fact suggests strongly that intramolecular crosslinking occurs with irradiation. The particle sizes calculated from the turbidity were 5~8 times larger than those determined by the electron micrograph. It was concluded that from the turbidimetric method the radius of micro-gel particle is determined, whereas from the electron micrograph one can measure only the radius of the small particle which forms the micro-gel particle.

INTRODUCTION

In Parts of VII⁽¹⁾ and VIII⁽²⁾ of this series we have reported that gelation of aqueous solutions of poly(vinyl alcohol) (denoted as PVA) takes place upon irradiation when the polymer concentration is so high that polymer molecules come into contact with each other. On the other hand, when the aqueous solution of PVA was irradiated below the critical concentration for the gel-formation, the solution became turbid and its viscosity was decreased simultaneously. It was then concluded that the turbidity of the irradiated solution was due to formation of micro-gel particles.

The object of the present study is to determine the size of the micro-gel particle by turbidity measurement and to obtain information about variation of the size of micro-gel during irradiation. Supplementarily we have also measured the size of the micro-gel by electron microscopy and compared the result with the size calculated turbidimetrically.

DETERMINATION OF PARTICLE SIZE

Recently one of the authors, with Hosono and Tamamura,⁽³⁾ has estimated the dimension of polymer latexes from turbidity measurement, basing on the electromagnetic theory derived originally by Mie⁽⁴⁾. It was shown by them that the turbidity method could be successfully applied for the determination of particle

桜田 一郎, 筏 義人

size. Since we apply here one of their methods and details of the method have been described elsewhere,^{3) 5) 6)} we outline only briefly the method for the determination of particle size.

Turbidity, τ , is defined as the extinction of light due to scattering. When the light passes through a turbid solution, the transmission, T , can be expressed by the equation :

$$T = \frac{I}{I_0} = e^{-\tau l} = e^{-Jcl} \quad (1)$$

Here I_0 is the incident and I the emergent intensity of light of wave length, λ , c the weight concentration of particle, J the scattering cross-section per gram and l the pass length of light. In the case of non-absorbing spherical particles, τ is related to the radius, r , and the density of particle, d , by the following equation :

$$\tau = \frac{3}{4} \frac{c}{d} \frac{K}{r} \quad (2)$$

where K is the scattering coefficient, *i.e.*, the ratio of the scattering cross-section of the particle to its geometric cross-section. K is known to be a function of r , λ and m . The relative refractive index, m , is defined as μ/μ_0 , where μ = refractive index of particle (polymer-rich phase) and μ_0 = refractive index of surrounding medium. Therefore, if the turbidity is measured at two different, suitable wave lengths, the following relation is obtained :

$$D.Q. = \frac{\tau_{\lambda_1}}{\tau_{\lambda_2}} = \frac{K_{\lambda_1}}{K_{\lambda_2}} = f(r, m) \quad (3)$$

where τ_{λ_1} and τ_{λ_2} are turbidities measured at λ_1 and λ_2 , respectively. $D.Q.$ is called the dispersion quotient⁷⁾. As is apparent from the equation (3), the radius of particle can be estimated from the $D.Q.$ values, when m is given.

In the case of micro-gel solution, m would be approximately equal to m' :

$$m' = \frac{\mu'}{\mu_0} \quad (4)$$

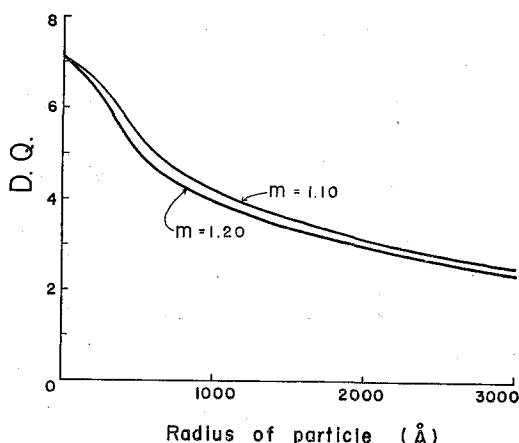


Fig. 1. Relation between the radius of particle and $D.Q.$ at $m=1.1$ and 1.20 ($\lambda_1=430m\mu$, $\lambda_2=700m\mu$).

Here μ' is the refractive index of the polymer molecule from which micro-gel particles are formed. Since $\mu' = \mu_{PVA} = 1.582$ and $\mu_0 = \mu_{H_2O} = 1.33$, m' is calculated to be 1.20. m is, therefore, expected to be equal to 1.20 or slightly smaller than 1.20. Fig. 1 shows the result calculated by Sakurada, Hosono and Tamanura³⁾, where $m = 1.20$ and 1.10. Consequently, with the aid of the curve of Fig. 1 the radius of micro-gel particle can be obtained graphically by measuring the turbidities at 430 m μ and 700 m μ .

EXPERIMENTAL

1) PVA Sample

The PVA samples used in this study are the same fractionated ones as described in Part VII¹⁾ of this series. The properties of samples are listed in Table 1.

Table 1. Characterization of sample PVA.

Sample	Sampl No.	$[\eta]^{a)}$	$D.P.^{b)}$	$C_c^{c)}$
I	N-1	1.48	4000	0.16%
II	F-5	0.80	1500	0.22%

^{a)} Limiting viscosity number of unirradiated PVA.

^{b)} Degree of polymerization of unirradiated PVA.

^{c)} Critical concentration for gel-formation.

2) Irradiation

The concentrations of solutions to be irradiated are 0.1 % for the sample I and 0.184 % for the sample II. After degassing, the solutions were irradiated at ambient temperature with γ -rays from a CO-60 source at a dose rate of 1.21×10^5 r/hr.

3) Viscosity and Turbidity Measurements

Viscosities of irradiated solution were measured at 30°C with an Ubbelohde-type viscometer. Turbidity measurements were carried out at room temperature with a photometer Type 7 manufactured by the Tokyokoden Company. The glass cell used is rectangular and the length which light traverses is 1.0 cm. In most cases the irradiated solutions were poured directly into the glass cell, but when the solutions were too dilute for the turbidity measurement, they were condensed to adequate polymer concentration before the turbidity measurement. The wave lengths chosen for the measurement were 430 m μ and 700 m μ .

4) Electron Microscopy

Samples for electron microscopy were obtained on the surface of poly (vinyl formal) film by casting the irradiated solution, to which lauryl sodium sulphate was added in order to avoid coagulation between micro-gel particles. After thorough evaporation of water the sample was shadowed with chromium.

RESULTS

1) Change in Viscosity by Irradiation

As mentioned earlier, solution viscosities were found to change in a peculiar manner on irradiation. Figs. 2 and 3 show the results of viscosity measurements

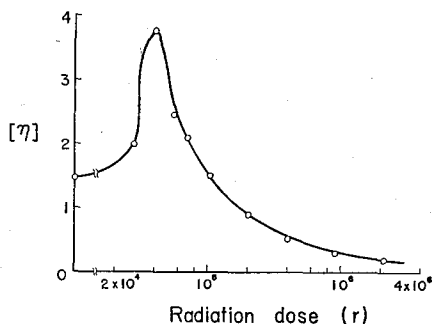


Fig. 2. Change in $[\eta]$ of sample I irradiated in 0.1% aqueous solution at 20°C.

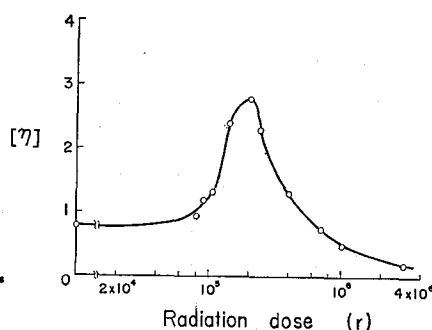


Fig. 3. Change in $[\eta]$ of sample II irradiated in 0.184% aqueous solution at 20°C.

for sample I irradiated in 0.1% solution and for sample II irradiated in 0.184% solution, respectively. In both cases, limiting viscosity number, $[\eta]$, is increased at an initial stage of irradiation, but after reaching a maximum it is decreased monotonously. When the radiation dose is higher than that corresponding to the maximum, the irradiated solutions become turbid. It was concluded in the previous paper²⁾ from several physical and chemical measurements that the decrease in viscosity and the turbidity of irradiated solution are attributed to formation of micro-gel particles. It should also be pointed out that the micro-gel is very stable even at a high temperature as 100°C.

2) An Example of Turbidity Measurements

Fig. 4 shows the result obtained by irradiation of 0.1% aqueous solution of

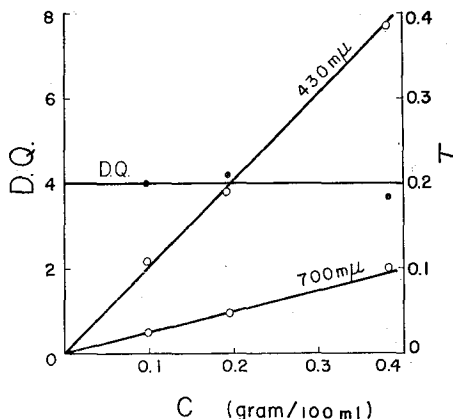


Fig. 4. D , Q , $\tau_{430m\mu}$ and $\tau_{700m\mu}$ as a function of polymer concentration for sample I irradiated with a dose of $2.2 \times 10^6 r$.

sample I with a dose of 2.2×10^5 r. The abscissa denotes the polymer concentration, where the turbidity was measured. As is clearly seen from Fig. 4, the Lambert-Beer law ($\tau \propto C$) holds over the range of the polymer concentration studied. The value of $D.Q.$ is practically independent of polymer concentration, as Deželić *et al*⁽⁶⁾ have also found.

3) Change in $D.Q.$ by Irradiation

The turbidities measured at 430 $m\mu$ and 700 $m\mu$ are given in Tables 2 and 3, together with the values of $D.Q.$ calculated from the turbidity data. It is seen that the $D.Q.$ value is decreased with increasing dose.

Table 2. Change in $D.Q.$, $\tau_{430m\mu}$ and $\tau_{700m\mu}$ of micro-gel obtained from sample I.

Exp. No.	Dose (r)	$\tau \times 100$		$D.Q.$
		430 $m\mu$	700 $m\mu$	
2	1.1×10^5	3.41	1.27	2.69
3	$2.0 \times "$	4.44	1.47	3.02
4	$4.0 \times "$	6.66	2.17	3.07
5	$9.0 \times "$	8.15	2.18	3.74
6	2.2×10^6	10.82	2.71	4.00
7	$6.0 \times "$	17.82	3.38	5.28

Table 3. Change in $D.Q.$, $\tau_{430m\mu}$ and $\tau_{700m\mu}$ of micro-gel obtained from sample II.

Exp. No.	Dose (r)	$\tau \times 100$		$D.Q.$
		430 $m\mu$	700 $m\mu$	
9	4.0×10^5	3.71	1.08	3.44
10	$6.0 \times "$	4.40	1.12	3.93
11	$9.0 \times "$	5.92	1.39	4.26
12	2.2×10^6	9.35	2.21	4.23

4) Radius of Micro-Gel

Radii of micro-gel particles estimated from $D.Q.$ values in Tables 2 and 3, using the curve ($m=1.20$) of Fig. 1, are tabulated in Tables 4 and 5. For comparison, radii determined from electron micrographs are also given in the tables. Examples of electron micrographs are shown in Fig. 5. Although at preparation of samples for electron microscopy the micro-gel particles could flatten and distort on drying⁽⁸⁾, any correction was not made for these.

Table 4. Radius of micro-gel particles obtained from sample I.

Exp. No.	Dose (r)	Radius (\AA)	
		from turbidity	from electron micrograph
2	1.1×10^5	2400	600
3	$2.0 \times "$	1900	500
4	$4.0 \times "$	1800	300
5	$9.0 \times "$	1100	200
6	2.2×10^6	1000	130
7	$6.0 \times "$	500	100

Table 5. Radius of micro-gel particles obtained from sample II.

Exp. No.	Dose (r)	Radius (\AA)	
		from turbidity	from electron micrograph
9	4.0×10^5	1400	400
10	$6.0 \times "$	1000	200
11	$9.0 \times "$	800	150
12	2.2×10^6	800	100

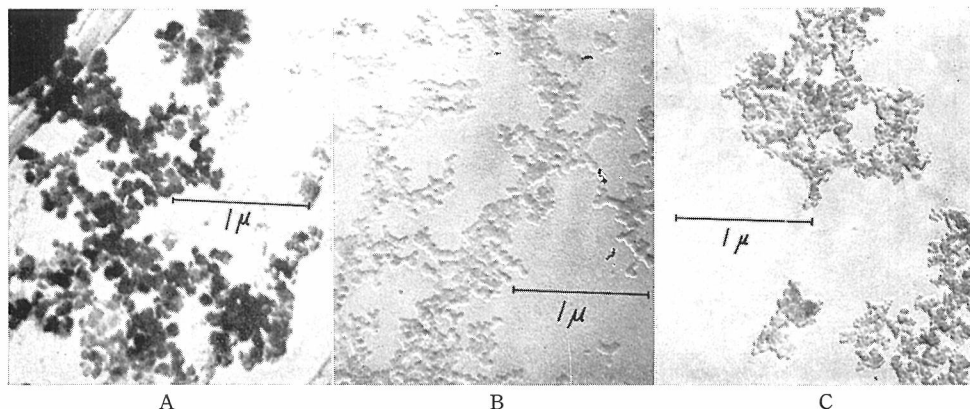


Fig. 5. Electron micrographs of sample I irradiated with various doses. (a) Exp. No. 2, (b) Exp. No. 4, and (c) Exp. No. 7 (see Table 4).

DISCUSSION

In the previous paper²⁾ it was concluded that the increase in viscosity at the initial stage of irradiation, for example, shown in Figs. 2 and 3 is due to formation of large particles as a result of intermolecular crosslinking among PVA molecules. This conclusion is surely supported by the present study, since the size of particles obtained by measuring the turbidity are markedly larger than that to be expected from one primary PVA molecule. The more important feature is that the size of micro-gel particles is decreased significantly as irradiation proceeds. This may be a strong evidence for occurring of intramolecular crosslinking which leads, hence, to decrease in viscosity. The difference in the degree of polymerization between sample I and sample II is expectedly reflected in the radius of micro-gel, that is, as is seen from Tables 4 and 5, the higher the degree of polymerization of the sample, the larger the radius of micro-gel particles formed.

As is obvious from Tables 4 and 5, the radius determined from electron micrographs is much smaller compared with those calculated from the turbidity measurement. Namely, the former is smaller than the latter by a factor of 3 to 8. Some causes might be pointed out for the discrepancy, since many assumptions were made to estimate the radius of micro-gel particles in both cases. For instance, when the turbidity method was applied to determine the radius, we assumed that the relative index, m , is 1.20 and that the particle is a sphere.

It was furthermore assumed that the micro-gel particles will flatten only to a negligible extent when the sample for electron micrographs is prepared. Of course, these assumptions are not necessarily correct, but it seems probable that they are not far from reality. It should be noted here that m will be roughly equal to 1.20 or slightly smaller than 1.20, (the radius is increased with decreasing m) and that the radius of flattened particle is larger than that of spherical particle. Therefore, the difference in radius calculated from the two methods may become more significant, if these corrections are effected. Besides the above assumptions, the distribution of particle size may also be taken into account. However, the ratio of the radius calculated from the two methods is probably not so considerably different from 2. In any case the difference in the radius determined from the turbidity and the electron micrograph in our study seems to be too large, though several authors have found that the agreement between the radius determined by the turbidity and by the electron microscopy is satisfactory^{3,8)} or the former is smaller than the latter⁹⁾.

This significant disagreement in the present case may be explained as follows. As is illustrated in Fig. 6, crosslinking may occur among the polymer

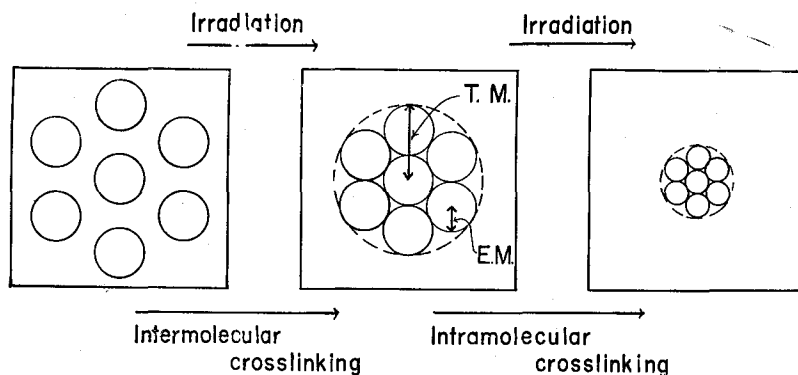


Fig. 6. Variation of micro-gel size by formation of inter- and intramolecular crosslinkings. The radii determined by turbidity measurement (T. M.) and electron micrograph (E. M.) are also indicated.

molecules at the initial stage of irradiation, that is, intermolecular crosslinking, while the intramolecular crosslinking may take place preferable on irradiation with sufficiently high dose. We have discussed inter- and intramolecular crosslinkings in the previous paper²⁾ in detail. It is then reasonable to suppose that the particle measured by the turbidity may be just the micro-gel particle which is formed from many primary particles and that the particle size determined from electron micrograph is the size of the primary particle. This supposition will also be supported by the following fact that the boundary of particles shown in the electron micrograph becomes obscure with increasing radiation dose, as is obvious from Fig. 5.

The authors wish to express their appreciation to Dr. M. Hosono for his useful suggestions, and to Mr. S. Tamamura for his help with the electron

microscopy work.

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